engineering proceedings

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Proceeding Paper

Enhanced Removal of Cr (VI) from Wastewater with Green and Low-Cost Nanomaterials Using a Fuzzy Inference System (FIS) and an Artificial Neural Network (ANN) †

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† Presented at the 2nd International Electronic Conference on Processes: Process Engineering—Current State and Future Trends (ECP 2023), 17–31 May 2023; Available online: https://ecp2023.sciforum.net/.

Abstract: In this study, an artificial neural network (ANN) and an adaptive neuro-fuzzy inference system (ANFIS) were used to predict the adsorption potential of an adsorbent for the removal of chromium (VI) from an aqueous solution. Four operational variables were studied to assess their impact on the adsorption study in the ANFIS model: initial Ni (II) concentration (mg/L), pH, contact duration (min), and adsorbent dose (mg/L). To build the ANN model, 70% of the data was used for training and 15% for testing and validation. The network was trained using feedforward propagation and the Levenberg–Marquardt algorithm. The regression coefficients (R^2) for the ANFIS and ANN models were 0.99 and 0.98, respectively. The results show good agreement between the model-predicted and experimental data, indicating that the models are appropriate and compatible. The RMSE between the predicted and observed removal percentage values for the ANFIS model was 0.008, whereas the RMSE for the ANN model was 0.06. The AARE values between the predicted and experimental removal percentage values for the ANFIS and ANN models were determined to be 0.009 and 0.045, respectively. The MSE vales between the predicted and experimental removal percentages for the ANFIS and ANN models were found to be 0.002 and 0.035, respectively. The optimum conditions were as follows: pH 6, an initial concentration of 275 mg/L, a contact time of 60 min, and a dosage of 12.5 mg/L; the absorption was 91.00%.

Keywords: artificial neural network; adaptive neuro-fuzzy inference system; wastewater; removal; Levenberg–Marquardt algorithm

Citation: Banza, M.; Seodigeng, T. Enhanced Removal of Cr (VI) from Wastewater with Green and Low-Cost Nanomaterials Using a Fuzzy Inference System (FIS) and an Artificial Neural Network (ANN). *Eng. Proc.* **2023**, *37*, 112. https://doi.org/10.3390/ECP2023-14677

Academic Editor: Antoni Sánchez

Published: 17 May 2023

1. Introduction

Heavy metals are primarily found in wastewater from various chemical industries, including steel production, chemical manufacturing, fertilizer, mining, pulp, and pesticides, as well as metallurgy, mining, coal power, leather industries, and the production of various polymers such as polyvinyl chloride [1]. The rapid rise of industrialization has significantly contributed to the release of pollutants into the environment. Since heavy metals are not biodegradable, they accumulate in human beings. Toxic heavy metals such as arsenic, chromium, copper, cadmium, lead, nickel, zinc, and mercury are critical in industrial wastewater treatment [2]. As the sixth most common transition metal, chromium is one of the metals with the highest abundance in the planet's crust. Crocoite, ferric chromite, and chrome ochre are mineral deposits that include metal chromium and other components. It is a well-known fact that this hazardous metal may be found in water [3]. Due to its necessity for human beings, Cr (III) is far less hazardous than Cr (VI). Nevertheless, Cr (VI) is extremely dangerous and may be present in different industrial effluents, leading to severe nausea, vomiting, lung congestion, and liver and kidney issues. Chromium metal is

used for chromate preparation, metal polishing, textile manufacturing, electroplating, and leather tanning [4].

To reduce the adverse effects of heavy metals on the public and the environment to an acceptable level, various techniques have been explored, including chemical oxidation/reduction, precipitation, ion exchange and adsorption, and membrane filtration [5]. Its drawbacks are its selectivity, saturation, temperature, pressure, expense, fouling, and specificity in the adsorption process. Adsorbents may also become contaminated and saturated, lowering their effectiveness and cost [6]. The procedure's efficiency also depends on the chemical composition of the compounds to be adsorbed and the adsorbent. As a result, many researchers are now focusing on creating bioresource adsorbents. Due to its renewability, biodegradability, and high stability, cellulose is a bioresource, and its derivatives have attracted the attention of several individuals. Due to their high affinity for different water pollutants among bio-based natural polymer nanocomposites, cellulose nanocrystals (CNCs) nanocomposites have been proven to be viable biosorbents for water purification [1].

An adaptive neuro-fuzzy inference systems (ANFIS) is a type of artificial intelligence (AI) that combines the learning skills of artificial neural networks (ANNs) with the reasoning abilities of fuzzy systems. As a result, it incorporates the advantages of both strategies into a single method. Instead of using only one technology, integrating fuzzy systems with ANNs is often more effective in engineering applications [7]. ANFIS is a powerful tool for modelling, mapping, forecasting, problem-solving, and data mining the interplay between input and output values to help explain non-linear behaviour in complex systems. The input and output of an ANFIS model are divided into two sections and connected by fuzzy rules into a network. It is commonly acknowledged as a technology because of its extensive ability to mimic non-linear variation, utility in predicting the effectiveness of various processes, and extrapolation based on historical data in various industries [8].

This study's primary objective was to prove that the modelling of Cr (VI) removal behaviour can be predicted using both models (ANN and ANFIS techniques). In the first step of the adsorption of Cr (VI) from an aqueous solution, cellulose nanocrystals are utilised as an adsorbent. The operational variables are the input data and include the initial concentrations, solution pH, contact time, and adsorbent dosage. Lastly, the predicted output data derived from the two models are compared to the experimental data output data.

2. Materials and Methods

The cellulose nanocrystals (CNCs) utilized in this study were extracted from waste papers via acid hydrolysis ($\geq$90%); cellulose nanocrystals were treated with succinic anhydride and EDTA (99%), and the pH of the solution was adjusted using NaOH (98%) and HCl (37%). The reactor containing CNCs was agitated at a speed of 180 rpm for 55 min, while 0.02 M EDTA tetrasodium salt was added to facilitate the reaction. The agitation period was then extended to 4 h, and 20 mL of hydrochloric acid was added. The modified product was centrifuged for 45 min at 450 rpm, washed to remove unreacted chemicals, and then centrifuged again until the pH was neutral. Further changes to the CNCs occurred after three hours of treatment with 0.02 M succinic anhydride at 25 °C. Batch investigations were conducted in 500 mL glass vials. Reactors with stoppered Erlenmeyer flasks carrying test solutions at room temperature (25 °C) with the appropriate Cr (VI) concentration, contact time, pH, and adsorbent dose levels. In each test, 50 mL of a solution with a particular concentration of Cr (VI) was added to the reactor. The pH of the solution was adjusted using diluted 0.01 M HCl or 0.01 M NaOH to maintain a constant pH throughout the experiment. Table 1 provides the range of process variables for the two models.

Table 1. The range of variables used for the models.

Input	Range	Output
1. pH	3–9	Removal percentage (%)
2. Concentration Ni (II)	50–500	
3. Time (min)	0–120	
4. dosage adsorbent (mg/L)	5–20	

3. Results and Discussion

Modular artificial neural networks and a neuro-fuzzy system were built with a NN toolbox using MATLAB 2019 mathematical software. All of the calculations needed to evaluate adsorption efficiency were performed using Origin 2019. The RMSE, AARE, and MSE of the training and prediction sets were also used to identify the two models and the parameter changes. To evaluate how well the model can predict results from experiments that have not yet been seen and were not used for training, we included 26 experimental runs that were randomly divided into training, validation, and test sets (20-3-3). Averaging was performed across all samples. R^2 is a standard statistical metric used to assess the extent to which experimental and model predictions vary. Figure 1 shows a three-layer system built with an input layer consisting of four neurons (Cr (VI) concentration, contact time, solution pH, and adsorbent dose), a hidden layer made up of nine different modes, and an output layer consisting of one neuron (4-6-1). The most widely used network, a back-propagation (BP-ANN), trains an algorithm for modelling experimental data using a first-order gradient descent method. This is a suitable method for minimizing mistakes throughout each cycle.

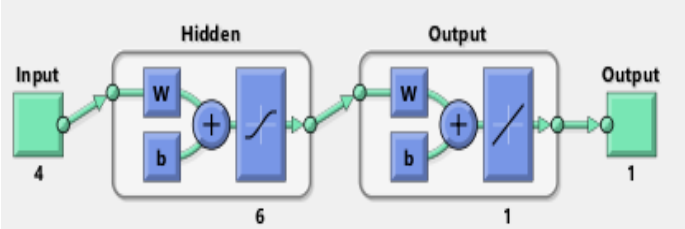

Figure 1. The architecture of the ANN model.

Figure 2 depicts how the network interacts with the training, testing, and validation data. The correlation coefficients for the training, testing, validation, and test data were found to be 0.999, 0.988, 0.972, and 0.988, respectively. The straight line also demonstrates a linear connection. The experimental (target) data and predicted (output) data from the model correlate. The results suggest good agreement between the actual data and the data predicted by the model.

A fuzzy system's membership parameters and rules are defined using a trial and error approach. A suitable model for the observed inputs and precise target values has to be developed using the ANFIS system. The product layer, normalized layer, fuzzy layer, defuzzy layer, and the final layer have all been identified as performing different tasks in this experiment (Figure 3).

In response to the four input parameters, which include three membership functions, the system creates 81 "and"-based rules (inputmf). After that, they are converted into output by being sent through the same amount of (outputmf). Figure 4 illustrates the ANFIS model's ability to predict data. (rule viewer). The optimum absorption conditions were as follows: pH 6, a starting concentration of 275 mg/L, a contact duration of 60 min, and a dosage of 12.5 mg/L; the absorption was 91.00%.

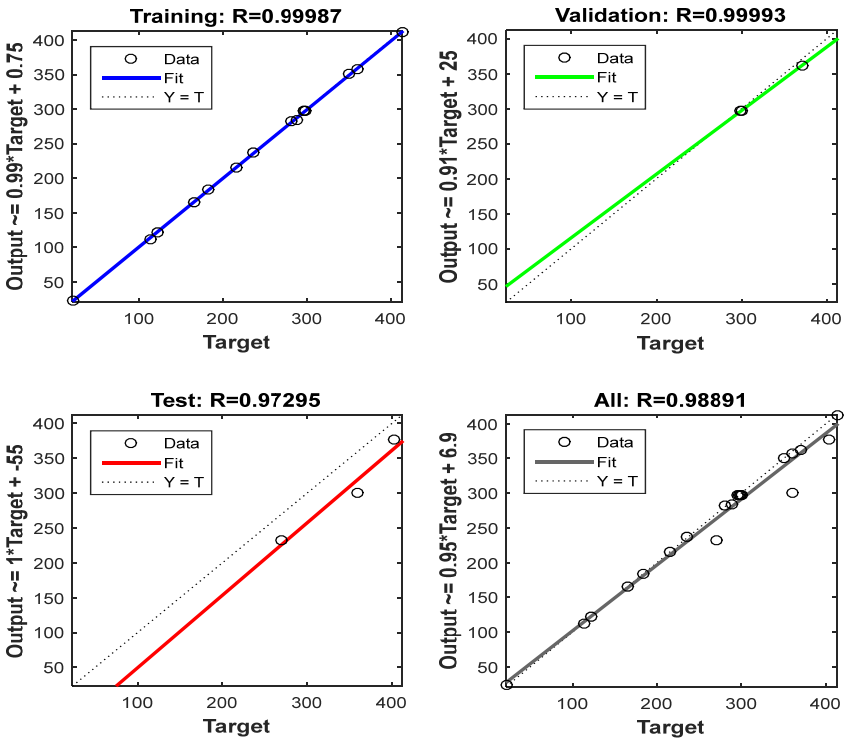

Figure 2. Training, validation, and testing for the Levenberg–Marquardt algorithm.

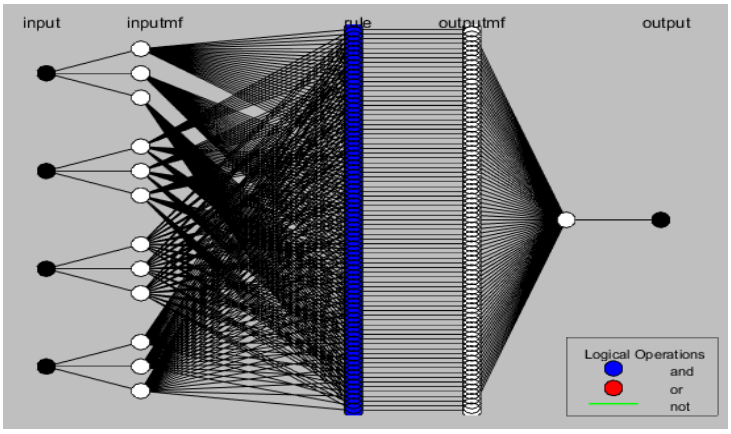

Figure 3. The architecture of the ANFIS model.

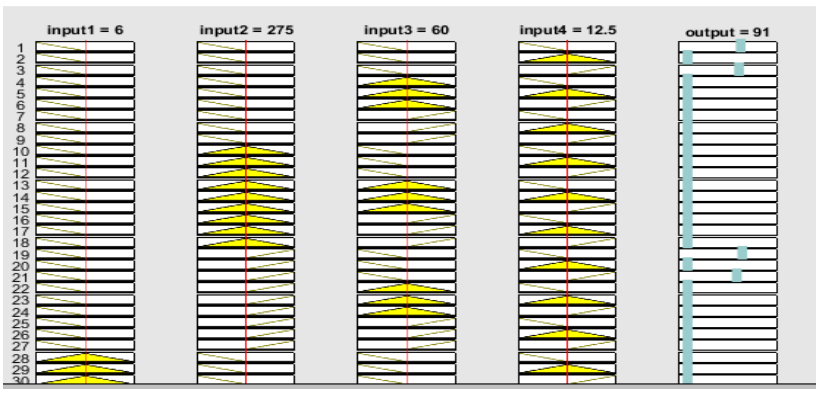

Figure 4. Rule viewer of the ANFIS model.

Table 2 compares the actual (experimental) data and the model-predicted data for the percentage of Cr (VI) removed using the CNCs. The findings show that both models can accurately predict the adsorption's features. Compared to the ANN model, the ANFIS model's RMSE, AARE, MSE, and R^2 values were determined to be 0.008, 0.09, 0.002, and 0.99, respectively, and the ANN values were found to be 0.06, 0.045, 0.035, and 0.98.

Table 2. Comparison of ANN and ANFIS model for Cr (VI) removal.

pH	Conc (mg/L)	Time (min)	Dosage (mg/L)	Actual (%)	ANN (%)	ANFIS (%)
6	250	120	10	92.00	92.2	92.7
6	250	60	10	93.01	92.7	93.07
3	50	0	20	79.52	78.05	78.9
9	50	120	5	82.94	84.82	83.89
3	500	0	20	75.51	75.28	76.14
9	50	0	20	72.47	71.90	71.12
6	250	60	10	93.92	93.24	93.82
6	250	60	10	93.97	93.51	93.77
9	50	120	20	76.70	76.28	77.27
3	50	0	5	81.54	81.25	81.54
6	50	60	10	84.92	84.85	84.73
3	500	0	5	84.08	83.25	83.79
9	500	0	20	71.05	71.02	71.08
9	500	120	20	75.05	74.56	74.28
6	250	60	10	93.91	93.24	92.71
RMSE (Root means square errors)					0.06	0.008
AARE (Absolute average relative errors)					0.045	0.09
MSE (Mean square errors)					0.035	0.035
R^2 (Regression coefficient)					0.98	0.99

4. Conclusions

This research study has not only achieved its primary objective but also created new areas for investigation. It could be possible to predict an adsorbent's adsorption capability. When ANFIS and ANN, two recently created models, are compared to one another, it becomes clear which model is better suited for use in the research area. The regression coefficients (R^2) for the ANFIS and ANN models were 0.99 and 0.98, respectively. The results demonstrate that the models are appropriate and compatible since there is an excellent fit between the experimental data and data predicted by the model. The ANFIS model had an RMSE of 0.008, whereas the ANN model had an RMSE of 0.06. The AARE valuues for the ANFIS and ANN models were determined to be 0.009 and 0.045, respectively. The MSE values for the ANFIS and ANN models were found to be 0.002 and 0.035, respectively.

Author Contributions: Conceptualisation, M.B.; methodology, M.B. and T.S.; software, M.B.; validation, M.B. and T.S.; formal analysis, M.B. and T.S.; investigation, M.B. and T.S.; resources, M.B. and T.S.; data curation, T.S.; writing—original draft preparation, M.B.; writing—review and editing, M.B. and T.S.; visualisation, M.B. and T.S.; project administration, T.S.; funding acquisition, T.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Acknowledgments: The authors would like to thank the Vaal University of Technology's Department of Chemical & Metallurgical Engineering for continuously providing access to operating facilities.

Conflicts of Interest: The authors declare no conflict of interest.

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